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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number: WO 92/12179
C08B 37/00, B01D 15/08	A1	(43) International Publication Date: 23 July 1992 (23.07.92)

(21) International Application Number: PCT/US91/09011

(22) International Filing Date: 3 December 1991 (03.12.91)

(30) Priority data:
640,322 4 January 1991 (04.01.91) US

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(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: PURIFICATION OF POLYDEXTROSE BY SIZE EXCLUSION CHROMATOGRAPHY

(57) Abstract

The present invention resides in an improved polydextrose composition with enhanced flavor characteristics that is useful as a sugarless bulking agent in a variety of food stuffs. Crude polydextrose solution is purified using size exclusion chromatography which removes substantially all of the undesirable manufacturing impurities and other sugar molecules that remain associated with untreated, commercially available polydextrose. These compounds are responsible for bitter tastes and musty off-notes which heretofore have rendered the product unfit for use in food products as a bulking agent. The purified compound now opens a new frontier of better tasting reduced calorie products.

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PURIFICATION OF POLYDEXTROSE BY SIZE EXCLUSION CHROMATOGRAPHY

FIELD OF THE INVENTION

This invention relates to purified polydextrose compositions in which most of the off-flavor constituents such as anhydroglucose have been removed by modified chromatographic techniques to provide an organoleptically acceptable polydextrose. More particularly, this invention provides a process for purifying polydextrose by size exclusion chromatography. The purified polydextrose prepared in accordance with this inventive method contains 1,6-anhydroglucose as well as mono- and disaccharides at concentrations below detectable levels or less than about 0.01% (W/W). The resulting product has substantially reduced off-tastes and is useful as a low calorie, sugarless bulking agent.

BACKGROUND OF THE INVENTION

Polydextrose is a water-soluble, low calorie non-cariogenic bulking agent. It is a randomly cross-linked glucan polymer produced through the acid-catalyzed condensation of glucose. U.S. Patent Nos. 3,766,165 and 3,876,794 to Rennhard detail the preparation of polymeric glucose and maltose products by anhydrous melt polymerization using non-volatile, edible, organic polycarboxylic acids as catalysts, cross-linking agents or polymerization activators.

Polydextrose is an essentially non-nutritive carbohydrate (approximately 1 calorie/gram) substitute. It provides a substitute for sugar and has many of the desired technological properties of sugar, but does not have the sweetness. This non-sweet bulking capability is advantageous where conventional sugar-based compositions have proven to be too sweet. Moreover, this non-sweet bulking capability is especially advantageous when used in combination with high intensity sweeteners to provide low-calorie food products having the desirable texture of

conventional sugar-containing food products without the calories associated with the sugar.

Polydextrose is commercially available in three forms. Polydextrose A, an amorphous, slightly acid fusible powder, Polydextrose N, a neutralized, light-colored 70% solution of Polydextrose A, and Polydextrose K, a neutralized powder form of Polydextrose A. As the polymerization process produces a mixture of polysaccharides and saccharide residuals, none of these products is a pure polydextrose product. All of these polydextrose products include a variety of low molecular weight compounds, such as glucose, sorbitol, citric acid and oligomers, which contribute to the calorie value of these products. In addition, all of the polydextrose products also include other low molecular weight compounds such as 1,6-anhydroglucose (levoglucosan) and 5-hydroxymethylfurfural which give these products a bitter taste and musty off-flavor. Although these low molecular weight compounds are found in polydextrose products only in small amounts (1,6-anhydroglucose, about 4%, bitter taste) (5-hydroxymethylfurfural, about 0.1%, musty off-flavor), those amounts are significant enough to negatively impact on the usefulness of polydextrose in most food products when polydextrose is present in medium to high levels.

U.S. Patent No. 4,622,233 to Torres discloses a first method of treating polydextrose by decolorizing it with a bleaching agent and thereafter purifying the decolorized material. A further method disclosed and claimed in the Torres '233 disclosure for reducing color, glucose content and anhydroglucose content of Type A polydextrose includes the following steps: (a) contacting a 60-70% (W/W) aqueous solution of polydextrose Type A with a food-approved bleaching agent at a temperature of 25°-90°C and a pH of about 2.5 to about 9.0; (b) adjusting the pH of the product of step (a), if about 7, to about 6; (c) adding one or more of the solvents selected from the group consisting of methanol, ethanol and ethylacetate such that said solvent includes 50-80%

(W/W) of the mixture; and (d) filtering the final product, and, if desired, drying. The Torres '233 patent ties decoloration to purification which is not necessary. Moreover, decoloration can be an undesired products requirement and condition which produces its own additional problems. For example, when the polydextrose purified by the Torres '233 method is subjected to high heating, such as in cooking, the coloring returns to the substance. In addition, the bleaching step leaves residuals which are difficult to remove. Furthermore, extra steps are required by Torres which require additional time, handling, and energy.

U.S. Application Serial No. 043,793, filed April 29, 1987, entitled "Method of Purifying Polydextrose and Composition Containing Same" and assigned to Warner-Lambert Company, assignee of the present application, discloses a process for providing a purified, unbleached polydextrose products wherein an aqueous solution of polydextrose in a concentration of from about 10% to about 90% is intimately contacted with a polar organic solvent such as ethanol or acetone. The ratio of polydextrose to solvent is from about 5% to about 45% by weight of polydextrose to about 35% to about 85% by weight of solvent. The mixture is then allowed to equilibrate to form a substantially contaminant-containing fraction and a substantially polydextrose-containing fraction. The fractions are then separated for use of the polydextrose-containing fraction.

U.S. Patent No. 4,956,458 to Bunick et al. also assigned to the Warner-Lambert Co. discloses the use of reverse osmosis technology in the removal of small molecular weight compounds to produce a purified polydextrose product. The reverse osmosis membrane allows for the selective removal of these impurities without the need for highly volatile organic solvents. The purification process results in high yields of the purified polydextrose compositions. In essence, an aqueous solution of commercially available polydextrose

is filtered by pressing it tangentially over a porous cellulose acetate membrane at high pressure. The membrane removes the bitter off-tastes that are due to the presence of 1,6-anhydroglucose and the 5-hydroxymethylfurfural impurities as well as glucose, sorbitol, citric acid and the like.

U.S. Patent No. 4,104,078 to Barker et al. discloses the separation of dextrans of different molecular weights into two fractions by column chromatography. The dextrans are first dissolved in an organic solvent which is then passed through a sequential chromatographic column which contains a suitable packing material and is rotated thereby producing two separate dextran fractions, one moving faster than the other through the material. The two fractions are eventually separated into distinct solutions which may then be collected.

EPA 0,010,769 to Ando et al. discloses a means of separating small molecular weight compounds by adsorption in a chromatographic column. Aqueous solutions containing fructose, glucose and high fructose corn syrup (HFCS) are passed through columns containing alkaline earth metal absorbants, calcium salt type absorbants or cation exchange resins. The purified compound is absorbed onto the packing material while the small molecular weight contaminants pass through or vice versa, depending upon the material used.

EPA 0,342,629 to Tanimura et al. discloses the separation and purification of sugar solutions by using cation exchange chromatography. The chromatographic apparatus is divided into four zones, i.e., an adsorption zone, a refining zone, a desorption zone and a concentration zone. The various sugars of different molecular weights are adsorbed, concentrated and refined in different zones depending on the cation exchange resin used therein.

EPA 0,101,304 to G. Gerhold discloses separation of a component such as fructose and glucose from a mixture of these and other components by creating a unidirectional fluid flow system through a number of

zones comprised of absorbant chambers through which the components travel at different rates. A component concentration established within these zones as inlet and outlet fluids comprised of feed and displacement fluids effect the physical separation of the sugar components based on molecular size.

EPA 0.279,946 to Ando et al. discloses the semi-continuous chromatographic separation of oligasaccharides using a cation exchange resin absorbant. The oligosaccharides are separated according to their affinity for the absorbant into constituent fractions which are separately withdrawn. The oligasaccharide mixture is repeatedly passed through the system in a cycle of supply, desorption and fluid circulation.

It is an object of the present invention to provide a sugarless polydextrose composition that is substantially tasteless and useful as a bulking agent or sugar replacement when combined with low calorie high intensity sweeteners in low calorie foodstuffs. More particularly, it is a further object of the present invention to provide a purified polydextrose composition in which the components responsible for the bitter, musty off tastes inherent in commercially available polydextrose have been removed. Specifically, it is an object of the present invention to provide a purified, sugarless polydextrose bulking composition, useful in the incorporation of a variety of reduced calorie food applications, in which low molecular compounds responsible for the musty, bitter off tastes have been removed by size exclusion chromatography.

SUMMARY OF THE INVENTION

A substantially tasteless, purified polydextrose composition is obtained through the use of size exclusion chromatography in which low molecular weight components such as mono- and disaccharides as well as 1,6-anhydroglucose are removed. These impurities which greatly detract from the usefulness of commercial polydextrose as a bulking agent in low calorie foods are

removed based on the molecular size of the individual components.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic flow diagram of the size exclusion chromatography process used to purify the improved polydextrose compounds of the present invention.

Fig. 3 is a chart showing the amount of polydextrose recovered after nine (9) runs expressed as a percentage by weight of the feed solution and the relative amounts of contaminents removed expressed a a percentage of the total amount existing in the original, unpurified feed solution.

Fig. 4 is a graph depicting relative sensory evaluation scores comparing the purified polydextrose compositions of the present invention with unpurified polydextrose.

DETAILED DESCRIPTION OF THE INVENTION

Size exclusion chromatography is a separatory process which separates chemical components based on the size of their molecules. In chromatographic processes in general, solutions of materials are passed through a cylindrical column which is filled with a packing, for which the constituents have an affinity which may be chemical, physical, or geometric. The various chemical species present in the solution are entrapped into and subsequently released from the chromatographic packing. This entrapment takes place by molecules of solute entering the pores of the packing. Molecules larger than the pore diameter cannot enter these pores and emerge quickly from the column, whereas smaller molecules enter the pores of the packing, and take longer to make their way through the column. The rates of entrapment and subsequent release vary from component to component, therefore giving rise to the phenomenon of separation by size exclusion chromatography.

It is believed that a number of key impurities are responsible for the bitter and unpleasant tastes that are associated with commercially available polydextrose. Unfortunately these are intimately associated with the polydextrose molecule per se and these are not easily dissociated therefrom as borne out by the prior art. This is particularly true in terms of a commercial purification process.

The manufacturing contaminants or impurities responsible for the off tastes consist generally of glucose, sorbitol, citric acid, 1,6-anhydroglucose, 5-hydroxymethylfurfural and other low molecular weight compounds and oligomers of unspecified origin. These are removed by feeding a polydextrose solution into a chromatographic column packed with a material such as a strong cation exchange resin. Suitable strong cation exchange resins are the hydrogen or metal ion forms of SM51 of Alcoa Separation Technologies, (Adsep) Rockford, Ill. Other suitable resins are Amberlite XE364R, 200 and IR-122 from Rohm & Haas, Phila., Penna, and XUS-40197 from the Dow Chemical Co., Midland, Mich. The solution is passed through the material for a sufficient time to remove these impurities yet not adversely affect the taste of the final polydextrose product. The larger polydextrose molecules are too large to enter the pores of the resin while the smaller molecular weight compounds that make up the impurities can enter and thereby take a longer period of time to pass through.

Referring now to Figure 1, the size exclusion chromatography process consists of a feed tank 1 in which the crude, commercial grade polydextrose solution is entered into the system. The concentration of this initial polydextrose feed can range from about 5% to about 70%, preferably from about 15% to about 50% and most preferably from about 20% to about 40% dissolved solids in aqueous solution by weight. However, in light of the fact that the size exclusion chromatographic column may be run as a continuous process, the total weights of the various feeds are not critical as are

their flow rates through the system. A feed pump 2 drives the polydextrose solution into a number of chromatography columns 4 while a circulation pump 3 agitates the solution and continuously passes it throughout the chromatographic packing and provides a driving force for penetrating the pores and interstices of the core exchange resin packing.

The number of chromatography columns 4 utilized may vary and may generally be determined by one skilled in the art according to the amount of crude polydextrose solution to be treated and any space limitations that may exist. For example, the more columns utilized in the system, the less the overall height necessary for each. Since the polydextrose solution is fed as a uniform flow throughout, a series of columns will effectively function as one.

The temperature at which the polydextrose solution is maintained may range anywhere from about 10°C to about 80°C, preferably 45°C to about 60°C and most preferably about 50°C for the greatest degree or efficiency of separation. The crude polydextrose feed solution is fed into the system at a rate of from about 2.0 to about 10.0 ml./min., preferably 3.0 to about 5.0 ml./min. and most preferably, 3.5 ml./min.

Once the polydextrose feed solution enters the size exclusion chromatography columns, a circulation pump 3 agitates the solution in and about the pores of the resin material at a rate of from about 20.0 to about 80.0 ml./min., preferably 30.0 to about 50.0 ml./min. and most preferably about 40.0 ml./min. The separation may be run as a continuous process and therefore a particular feed solution may be run through the columns any number of times depending on the concentration of the polydextrose feed solution to be treated and the purity desired for the final product.

A second feed tank 7, introduces a flow of water into the system after sufficient time has passed for the separation of materials in the columns. This flow is essentially a desorbtion step driven by pump 6 that

forces the water through the columns 4 thereby removing all the smaller molecular weight contaminants which flow through the pores of the resin material. The desorption flow rate may range from about 10.0 to about 50.0 ml./min., preferably from about 10.0 to about 20.0 ml./min. and most preferably about 16 ml./min.

Switching valves 9 control intake and out take of both the desorb feed with the smaller molecular impurities and the purified polydextrose product once the waste effluent has been removed. These are critical in the process in providing a proper location for feed and product entry/withdrawal which is important since the location of peak concentrations of the different molecular contaminants changes with time. By opening and closing the valves at suitable times according to the concentration of the polydextrose feed solution, waste product contained in the desorb feed is removed from the columns and expelled to a waste material container 11. It is important to remove the contaminants at a consistent rate in order to prevent a backup in the columns whereby the small molecular weight contaminants are bunched together thereby clogging the resin pores. The desorb feed is therefore removed at a rate of from about 5.0 to about 30.0 ml./min., preferably 8.0 to about 15.0 ml./min. and most preferably withdrawn at a rate of about 11.0 ml./min.

Once the small molecular weight waste effluent is removed, the purified polydextrose can be washed from the resins using a suitable non-organic solvent which, when the outlet valves 9 are opened and closed accordingly, will be pumped out of the columns and onward to a purified polydextrose retention tank 10. The withdrawal rate, although not critical to the processing parameters of the invention, tends to yield the best results in a range of from about 5.0 to about 40 ml./min., preferably from about 5.0 to 10 ml./min. and most preferably at a rate of about 8.5 ml./min. Again, additional runs as a continuous process can be achieved through proper valve 9 settings and will tend to yield an even greater purified

product. The flow rates set forth above all produce a desired product and optimum values may vary depending upon the concentration of the initial crude polydextrose feed, the temperatures at which the process is run and the length of time each cycle is complete.

The process is run as a continuous operation and the amount of time the polydextrose is passed through or spends in the system is variable since continuous operations are time invariant. Residence time, one means for defining the time concept is calculated by dividing the volume of the continuous operation by the volumetric flow rate of the system utilized. The approximate volume of the system utilized in the following examples was 250 mls.

The following examples are provided in order to illustrate possible ways to practice the concept of the present invention. Whereas the examples provided deal with a bench type, laboratory scale process and amounts are given accordingly, scale up to pilot plant and commercial operations would utilize the materials cited in the same proportions and ratios but in larger quantities. They are for illustration only, and it is realized that many variables exist that may be changed in one way or another, and therefore any changes and minor variations in the processing parameters disclosed therein are considered to be within the spirit and scope of the present invention as later defined by the claims.

Example 1

The purified polydextrose composition was prepared by size exclusion chromatography and analyzed by a high pressure performance liquid chromatography (HPLC). A 50% crude polydextrose solution (dissolved solids in aqueous solution by weight) was pumped at a feed rate of 5.0 ml./min. at a pseudo-continuous mode through a system of ten (10) strong cation exchange resin columns measuring 2½ ft. x 1 in. diameter. The columns have two feed lines and two product take-off lines as disclosed in Fig. 1 which are positioned to correspond to the appropriate

position of the wave fronts in the column. As the wave fronts travel, the feed and withdrawal parts are repositioned accordingly thus achieving an essentially continuous flow regime from a fundamental batch unit operation.

The purification process was run at approximately 50°C with a circulation rate within the columns of 45 ml./min. The polydextrose solution was purified for approximately three (3) days. Concurrently, distilled (H_2O) water was used to flush out and desorb the small molecular weight impurities held by the resin. The initial components to pass through the column are expectedly purified polydextrose which is immediately retained in the purified container. The desorption step was carried out at 15 ml./min. continuously throughout the run. The purified polydextrose product was then extracted and collected from packing and analyzed.

Referring to Figure 2, the polydextrose feed solution was analyzed as the various components passed through the column. Clearly, the purified polydextrose whose molecules were too large to be retained by the strong cationic resin packing passed through the column and is seen as the first peak. The components attributing to the off notes and bitter tastes are detected later in the desorption was as three (3) peaks almost superimposed over one another appears in bed volumes of 0.5 to about 0.85 liters. These were separated further and as noted by the graph consist of sorbitol, dextrose and 1, 6,- anhydroglucose.

Example 2

Purified polydextrose compositions were prepared using size exclusion chromatography and an unpurified feed solution with a forty percent (40%) polydextrose concentration. Referring again to Fig. 1, a four (4) liter reservoir 1 was filled and pumped into the system at a rate of 3.5 mls./min. Immediately thereafter, a desorb water feed 7 was pumped into the system at 16 mls./min. Once the column was filled, the circulation

pump 3, set at 40 mls./min. was turned on and purified polydextrose was then withdrawn by opening the appropriate withdrawal valves 9 in the size exclusion chromatography columns comprising a strong cationic exchange resin such as Adsep SM51. The residence time that a given sample spends in the column is calculated by dividing the volume of the continuous purification operation by the volumetric flow rate. A crude feed rate of 3.5 mls./min. will have a residence time of 72 minutes while a desorb water feed of 16 ml./min. will have a residence time of 16 mins. The process was run continuously at a temperature of about 50°C and purified polydextrose was withdrawn at regular intervals.

The bed volumes withdrawn were analyzed by HPLC and Figure 2 clearly shows the separation of the purified product from the 1,6-anhydroglucose, dextrose and sorbitol contaminents.

Example 3

The purified polydextrose composition isolated in Example 1 was subjected to an expert taste testing panel and compared with unpurified polydextrose samples commercially available on the market. The purified and unpurified polydextrose samples were incorporated into a conventional boiled hard candy with the exception that no sweetener, flour, color or acid was added so that any taste perception would be due primarily to that of the polydextrose. Referring to Fig. 4, the relative degree of likeness is shown to be more than 2:1 in favor of the candies mede with the purified bulking agent.

What We Claim is:

1. An improved sugarless polydextrose composition with substantially enhanced flavor characteristics prepared by:

a) feeding a crude polydextrose solution at a suitable temperature and pressure into a size exclusion chromatography column.

b) circulating said polydextrose solution within said column for a suitable period of time.

c) desorbing said column with water to remove any impurities and;

d) collecting and concentrating the purified polydextrose retentate.

2. The improved polydextrose composition of claim 1 wherein said size exclusion chromatography column is comprised of a strong cationic exchange resin.

3. The improved polydextrose composition of claim 2 wherein said strong cationic exchange resin is selected from the group consisting of hydrogen or metal ion forms of Adsep SM51, Rohm & Haas Amberlite XE364R, Amberlite 200, Amberlite IR-122, Dow XUS-40197 and mixtures thereof.

4. The polydextrose composition of claim 3 wherein said impurities are selected from the group consisting of oligomers and small molecular weight compounds.

5. The polydextrose composition of claim 4 wherein said impurities are selected from the group consisting of 1,6 anhydroglucose, and low molecular weight polysaccharides.

6. The polydextrose composition of claim 5 wherein said low molecular weight polysaccharides are selected from the group consisting of dextrose, sorbitol and mannitol.

7. The polydextrose composition of claim 6 wherein the concentration of polydextrose in the crude polydextrose feed solution is from about 5% to about 70% dissolved solids by weight.

8. The polydextrose composition of claim 7 wherein said concentration of polydextrose is from about 15% to about 50% dissolved solids by weight.

9. The polydextrose composition of claim 8 wherein said concentration of polydextrose is from about 20% to about 40% dissolved solids by weight.

10. The polydextrose composition of claim 9 wherein said crude polydextrose solution is fed into the size exclusion chromatography columns in a continuous manner.

11. The polydextrose composition of claim 9 wherein said crude polydextrose solution is fed into the size exclusion chromatography columns in a batch manner.

12. The polydextrose composition of claims 10 or 11 wherein said enhanced flavor characteristics are the substantial absence of bitter and musty off-tastes.

13. An improved polydextrose composition substantially free of sugar and processing contaminants responsible for bitter and undesirable taste characteristics.

14. The polydextrose composition of claim 13 wherein said processing contaminants consist of oligomers and small molecular weight polysaccharides.

15. The polydextrose composition of claim 14 wherein said small molecular weight polysaccharides are selected from the group consisting of sorbital, dextrose, and mannitol.

16. The polydextrose composition of claim 15 wherein said oligomers are selected from the group consisting of 1,6-anhydroglucose.

17. An improved polydextrose composition with substantially enhanced flavor characteristics useful as a bulking agent in food stuffs.

18. The polydextrose composition of claim 17 wherein said enhanced flavor characteristics are the absence of bitter taste and musty off-notes.

19. The polydextrose composition of claim 17 further comprising a high intensity sweetener.

20. The polydextrose composition of claim 19 wherein said high intensity sweetener is selected from the group consisting of saccharin, cyclamate, aspartame, acesulphame-K, talin, dihydrochalcone, sucralose, alitame, stevioside, monellin, and mixtures thereof.

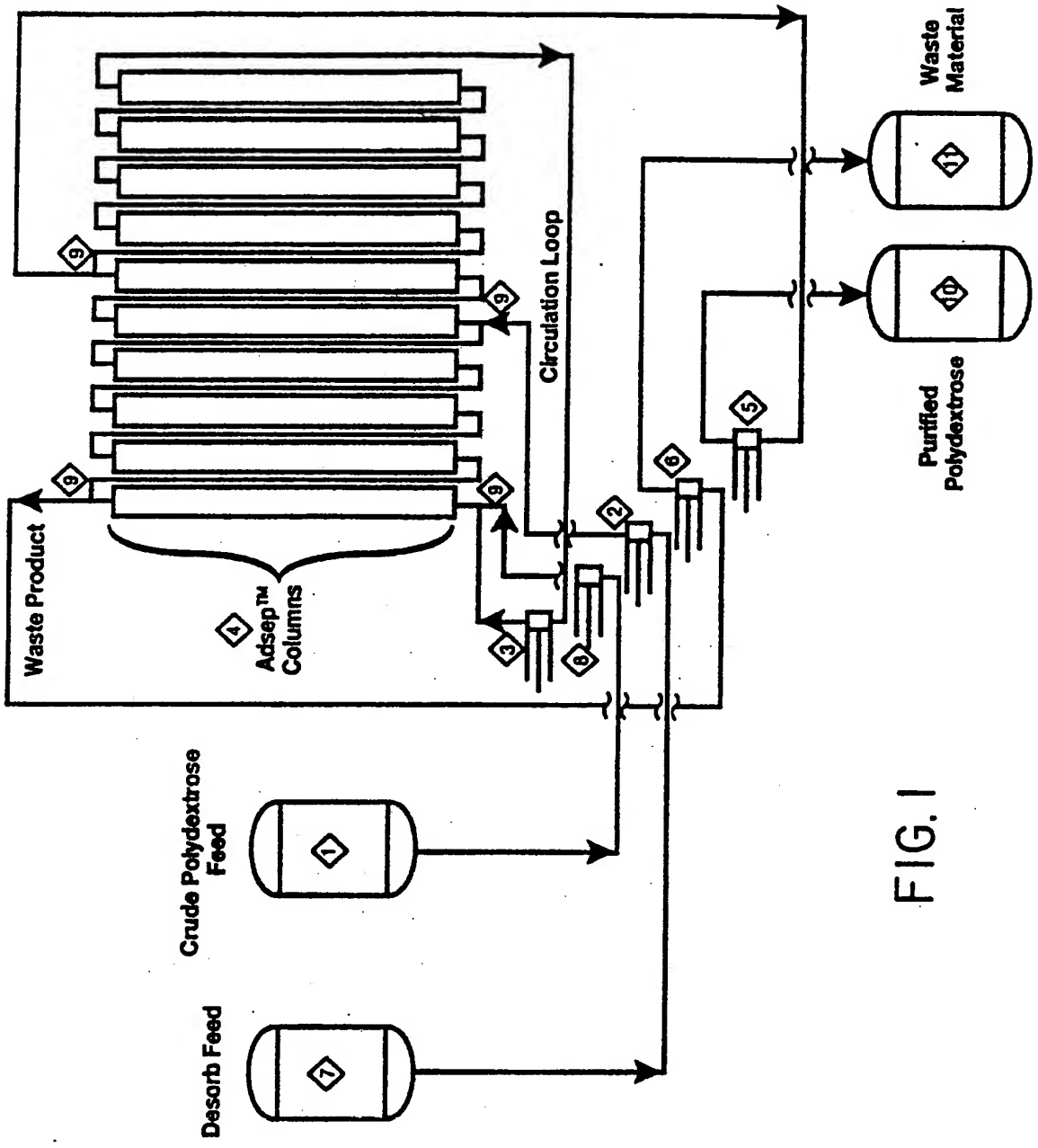

Waste Material
Purified Polydextrose
Circulation Loop
Waste Product
Adsep™ Columns
Crude Polydextrose Feed
Desorb Feed

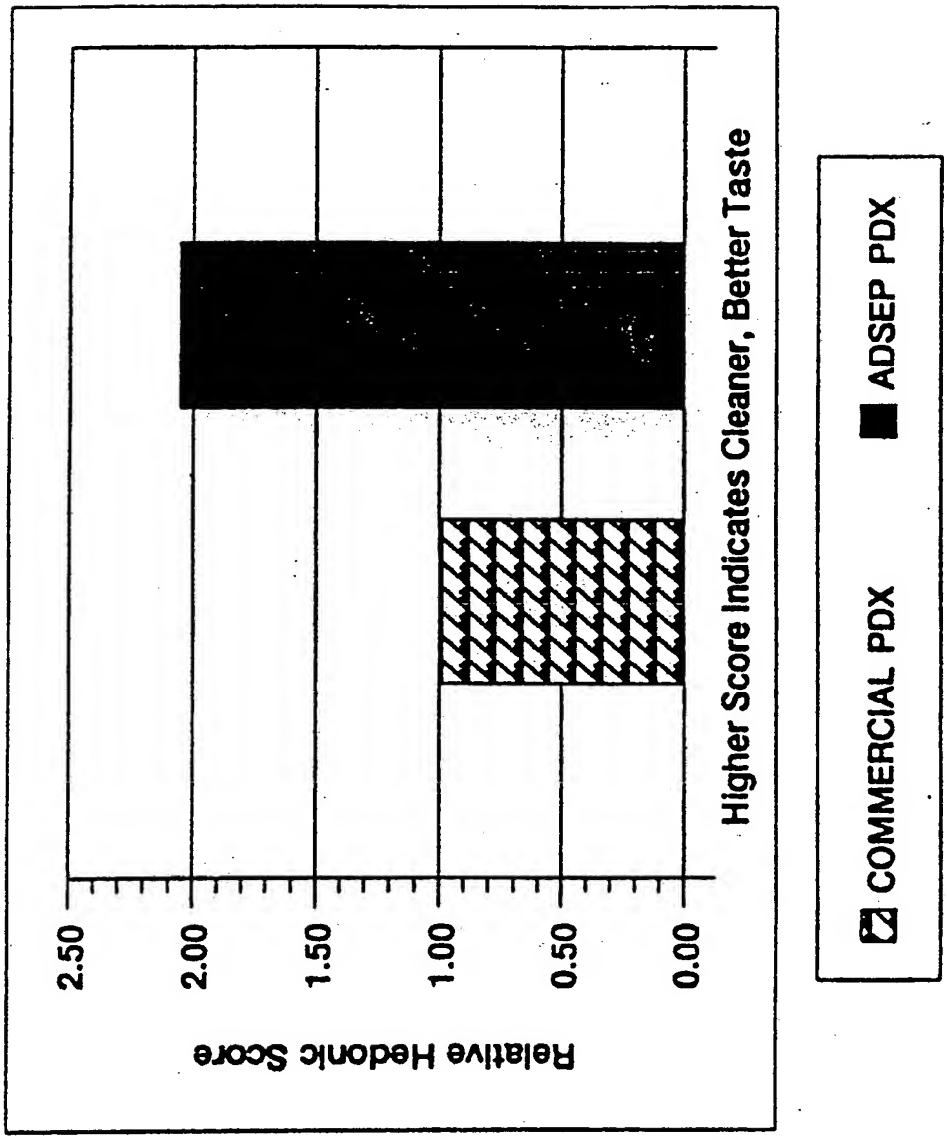
FIG. 1

FIG. 2

ADSEP LS POLYDEXTROSE RECOVERY AND CONTAMINANT REJECTION

# Sample	Polydextrose Recovery	% Rejection				
		Glucose	Sorbitol	1,6-Anhydroglucose	Unknown	Maltose
1	99	3	24	>99		
2	98	11	67	>99	>99	
3	97	76	86	68		
4	97	76	86	79	>99	
5	98	60	84	87	>99	
6	97	48	83	96	>99	
7	93	>99	>99	>99	>99	31
8	95	>99	>99	>99	>99	49
9	94	>99	>99	>99	>99	62

FIG. 3


Relative Hedonic Score
2.50
2.00
1.50
1.00
0.50
0.00
Higher Score Indicates Cleaner, Better Taste
COMMERCIAL PDX
ADSEP PDX

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/09011

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08B37/00; B01D15/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08B ; B01D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[10]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	EP,A,0 380 248 (PFIZER INC.) 1 August 1990 see claims 1-10; examples 2,3 ---	1-20
Y	US,A,3 756 919 (I.F. DEATON) 4 September 1973 see claims 6-9; example II ---	1-20
P,X	EP,A,0 458 748 (WARNER-LAMBERT COMPANY) 27 November 1991 see page 3, column 4, line 53 - page 4, column 5, line 29 ---	1-20
E	EP,A,0 473 333 (PFIZER INC.) 4 March 1992 see page 3, line 40 - line 43; claim 8 ---	1-20

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* Special categories of cited documents :[10]

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
19 MARCH 1992	24 MAR 1992
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	LENSEN H.W.M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CARBOHYDRATE POLYMERS. vol. 8, no. 2, 1 February 1988, BARKING GB pages 119 - 130; D. LECACHEUX ET AL.: 'PREPARATIVE FRACTIONATION OF NATURAL POLYSACCHARIDES BY SIZE EXCLUSION CHROMATOGRAPHY'	

A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 279 (C-257)(1716) 20 December 1984 & JP,A,59 148 794 (HAYASHIBARA SEIBUTSU KAGAKU KENKYUSHO K.K.) 25 August 1984 see abstract	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9109011
SA 54916

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0380248	01-08-90	AU-B- 606304	31-01-91
		AU-A- 4882090	09-08-90
		CA-A- 2008453	26-07-90
		JP-A- 2233702	17-09-90
US-A-3756919	04-09-73	None	
EP-A-0458748	27-11-91	None	
EP-A-0473333	04-03-92	None	

EPO FORM P079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82